

Near-infrared luminescence in bismuth-doped TlCl crystal

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Experimental and theoretical studies of spectral properties of crystalline TlCl:Bi are performed. Two broad near-infrared luminescence bands with a lifetime about 0.25 ms are observed: a strong band near 1.18 μm excited by 0.40, 0.45, 0.70 and 0.80 μm radiation, and a weak band at $\gtrsim 1.5 \mu\text{m}$ excited by 0.40 and 0.45 μm radiation. Computer modeling of Bi-related centers in TlCl lattice suggests that $\text{Bi}^+ \cdots \text{V}_{\text{Cl}}^-$ center (Bi^+ in Tl site and a negatively charged Cl vacancy in the nearest anion site) is most likely responsible for the IR luminescence.

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I. INTRODUCTION

For more than a decade bismuth-doped glasses and optical fibers attract a considerable interest due to broadband IR luminescence in the range of 1.0–1.7 μm used in fiber lasers and amplifiers (see e.g. the review [1]). Although the origin of IR luminescence is still not clear, recently the belief has been strengthened that subvalent Bi centers are responsible for the luminescence [2]. In our opinion, monovalent Bi centers are of a particular interest. Crystalline halides of monovalent metals are convenient as model hosts to study such centers. These crystals have a simple structure (primitive, $\text{Pm}\bar{3}\text{m}$, or face-centered, $\text{Fm}\bar{3}\text{m}$, cubic lattice). Bismuth can easily form monovalent substitutional centers in such lattice. Similar subvalent Tl and Pb centers in $\text{Fm}\bar{3}\text{m}$ crystals were studied extensively (e.g. Tl in KCl [3] and Pb in MF_2 ($\text{M} = \text{Ca}, \text{Sr}, \text{Ba}$) [4]). By analogy, the models of Bi-related centers in oxide glasses for fiber optics were suggested [5]. Subvalent Bi centers in cubic halide crystals were studied for the first time in BaF_2 [6] and then in CsI ($\text{Pm}\bar{3}\text{m}$) [7, 8].

In the present work we report the results of spectroscopic study and computer modeling of Bi-related centers in bismuth-doped TlCl crystal ($\text{Pm}\bar{3}\text{m}$).

II. EXPERIMENTAL

TlCl single crystals were grown by Bridgman-Stockbarger method as described in [9]. TlCl with a cationic impurities content of $\lesssim 1 \times 10^{-4}$ wt.% was used as an initial material. BiCl_3 (99.999 %, ultra dry) with concentration of 0.1–0.4 wt.% was used as dopant. Crystals were grown in nitrogen atmosphere (residual pressure of 10^{-2} mm Hg) in Pyrex glass ampules with a rate of

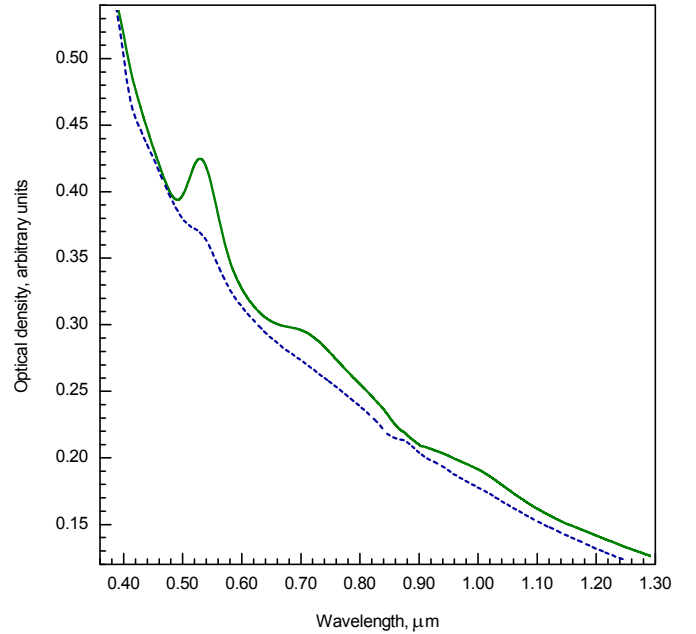


Figure 1. Optical density of TlCl:Bi crystals with a higher (solid line) and lower (dashed line) Bi content

$\lesssim 2$ mm/h. The interface–phase boundary was kept at 15–20 mm above the separating diaphragm. The temperatures of the upper and lower zones of a vertical furnace were held at 460°C (30°C above TlCl melting temperature) and at 350°C, respectively. Crystals of 22 mm diameter and 80–100 mm length were produced. For spectroscopic measurements 5 mm-thick plates were cut from the crystals, ground and polished. The measurements were carried out by using two samples with different total Bi content. The transmission spectra were measured by Perkin Elmer Lambda 900 spectrophotometer. The luminescence emission and excitation spectra, as well as the luminescence lifetimes were measured by Edinburgh

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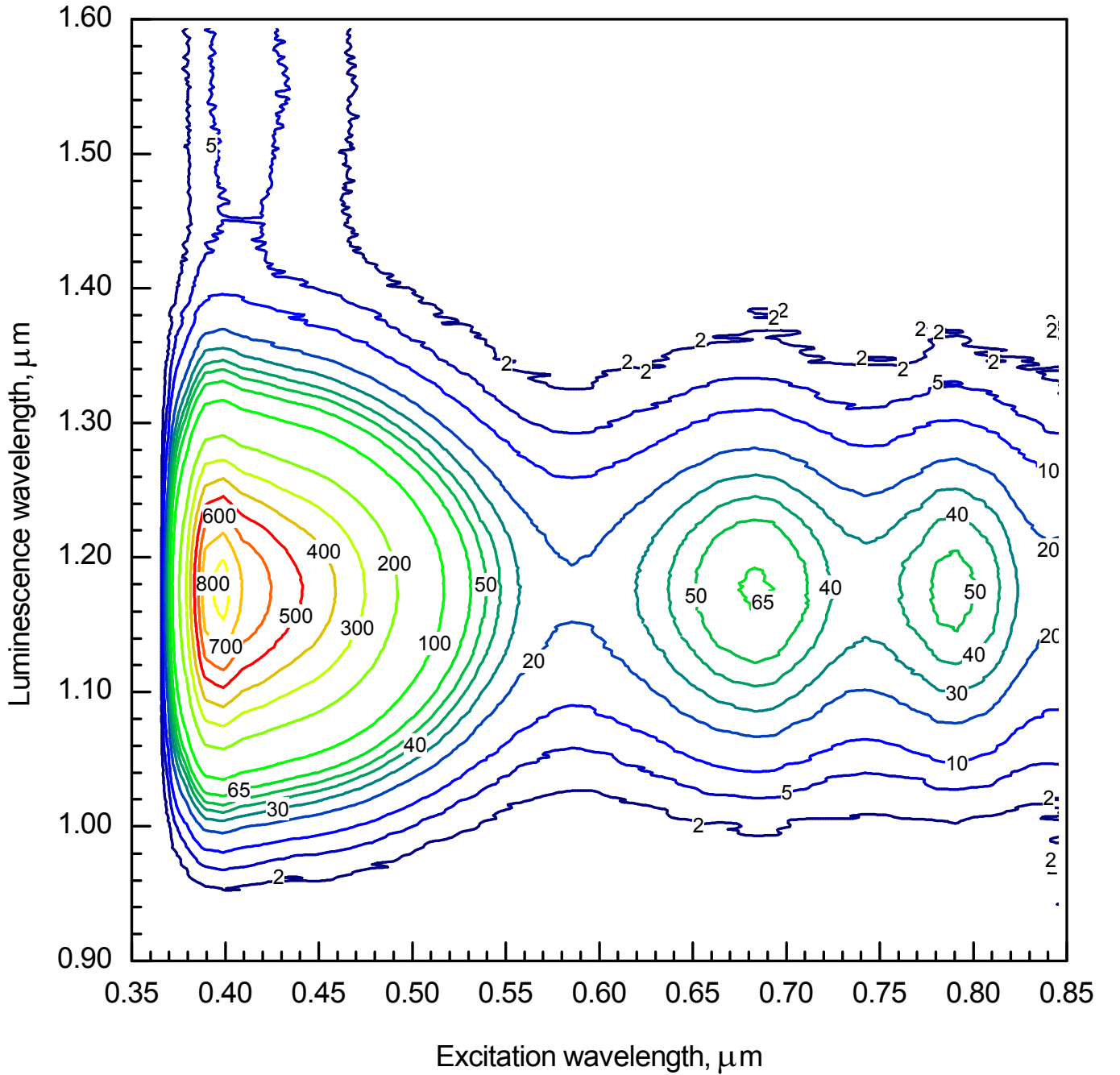


Figure 2. Bi-related luminescence in TlCl:Bi crystal (intensity is given in arbitrary units)

Photonics FLS 980 spectrometer.

One strong band near $0.53 \mu\text{m}$ and three weak bands near 0.45 , 0.72 , and $1.0 \mu\text{m}$ are observed in the absorption spectrum (Fig. 1). Two IR bands are observed in the luminescence spectrum (Fig. 2). The strong band near $1.18 \mu\text{m}$ with a half-width about $0.2 \mu\text{m}$ is excited in 0.40 , 0.45 , 0.70 , and $0.80 \mu\text{m}$ absorption bands. The weak band at $\approx 1.5 \mu\text{m}$ is excited in 0.40 and $0.45 \mu\text{m}$ absorption bands. The luminescence lifetime is 0.20 – 0.35 ms in

both IR bands. It should be emphasized that the luminescence excitation spectrum differs from the absorption spectrum, and that the absorption increases with Bi content (Fig. 1), as opposed to the IR luminescence.

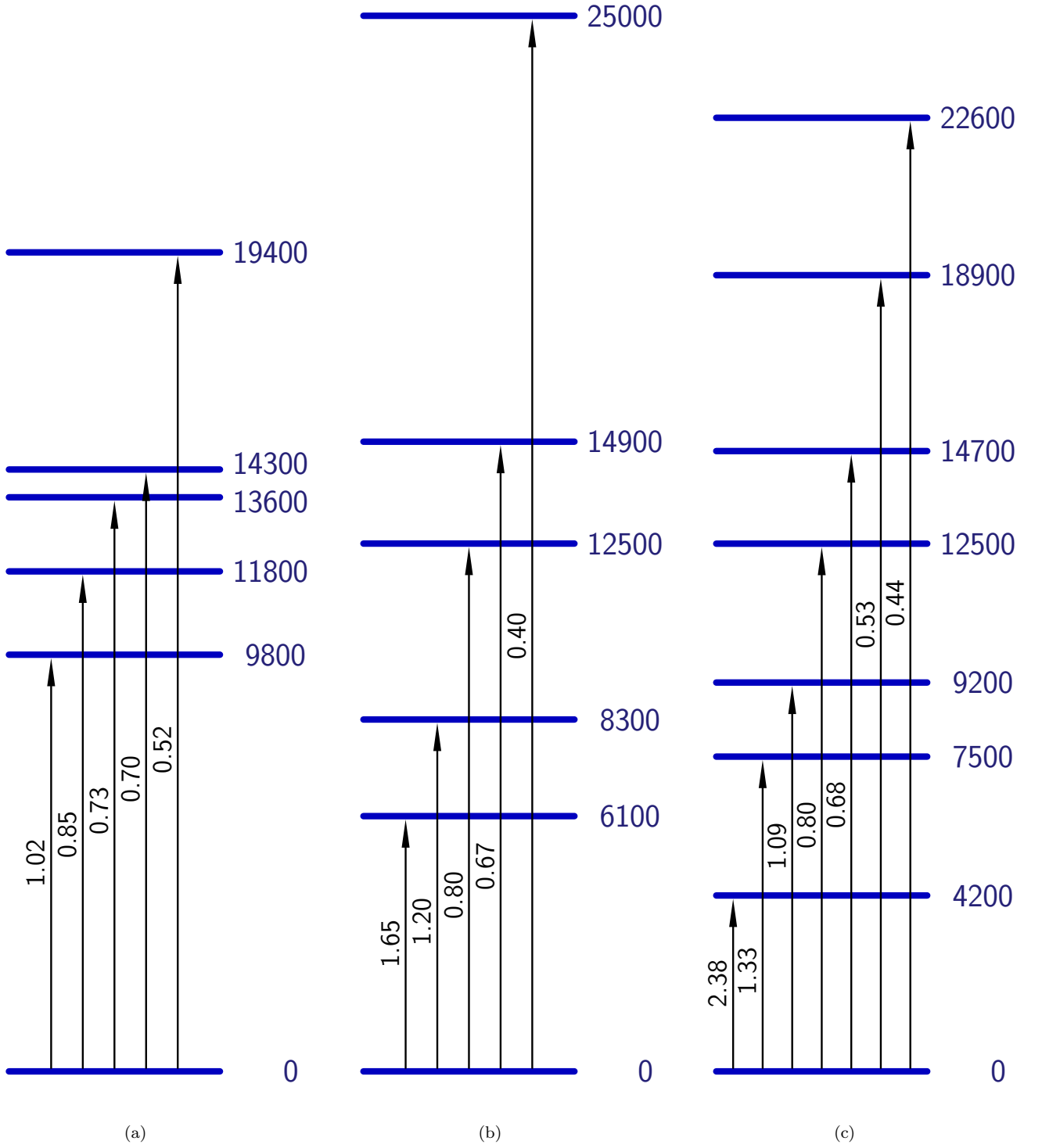


Figure 3. Calculated levels and transitions of Bi-related centers in TlCl:Bi crystal: (a) Bi^+ substitutional center, (b) $\text{Bi}^+ \cdots \text{V}_{\text{Cl}}^-$ complex, (c) Bi_2^+ dimer center (level energies are given in cm^{-1} , transition wavelengths in μm)

III. MODELING OF BISMUTH-RELATED CENTERS IN TLCL:BI

To understand the origin of the IR luminescence, we performed a computer simulation of the structure and

absorption spectra of several Bi-related centers possibly occurring in TlCl:Bi crystal. Firstly, monovalent Bi substitutional center, Bi^+ , was studied as the main form of Bi in TlCl. Further, $\text{Bi}^+ \cdots \text{V}_{\text{Cl}}^-$ complex formed by the Bi^+ center and negatively charged Cl vacancy in its first

coordination shell (in other words, both located in the neighboring sites of TlCl lattice) was modeled as a center similar to $\text{Tl}^0(1)$ center in KCl crystal [3]. And finally, dimer center, Bi_2^+ , formed by two Bi^+ substitutional centers in the nearest sites of TlCl cation sublattice with an extra electron, was chosen by analogy with the assumptions made in [7, 8] for CsI:Bi.

The modeling was performed in supercell approach. To model Bi^+ and $\text{Bi}^+ \cdots \text{V}_{\text{Cl}}^-$ centers, $3 \times 3 \times 3$ TlCl supercell containing 54 atoms was chosen, and $3 \times 3 \times 4$ supercell with 72 atoms was used for Bi_2^+ . In the central region of the supercell certain Tl atoms were substituted by Bi atoms and an anion vacancy was formed by a removal of one Cl atom. Charged centers were simulated changing the total number of electrons in the supercell. Equilibrium configurations of the centers were found by a complete optimization of the supercell parameters and atomic positions with the gradient method. All calculations were performed using Quantum-Espresso package [10] in the plane wave basis in the generalized gradient approximation of density functional theory (DFT) with ultra-soft pseudopotentials built with PBE functional [11]. To test the approach, we calculated TlCl lattice parameters both for TlCl unit cell and for the supercells with both atomic positions and cell parameters completely optimized. The results convergence was tested with respect to the plane wave cutoff energy and to the k points grid.

Configuration of the Bi-related centers calculated by this means was used to calculate the absorption spectra of the centers by the Bethe-Salpeter equation method based on all-electron full-potential linearized augmented-plane wave approach. The calculation was performed using Elk code [12] in the DFT local spin density approximation with PW-CA functional [13, 14]. Spin-orbit interaction essential for bismuth-containing systems was taken into account. Scissor correction was applied in transition energies calculation with the scissor value found using modified Becke-Johnson exchange-correlation potential [15–17]. Convergence of the results was tested with respect to plane wave cutoff energy, to the angular momentum cutoff for the muffin-tin density and potential, and to the k points grid choice.

Configurational coordinate diagrams of the Bi-related centers were calculated in a simple model restricted to the lowest excited states with a displacement of Bi atom(s) along [111] axis for Bi^+ and $\text{Bi}^+ \cdots \text{V}_{\text{Cl}}^-$ centers and along [001] axis for Bi_2^+ center. In spite of the fact that the model is inherently approximate, it shows that in all three centers studied the Stokes shift corresponding to a transition from the first excited state to the ground one do not exceed the accuracy of the excited state energy calculation. Hence it is reasonable enough to estimate the IR luminescence wavelengths by taking the Stokes shift to be zero.

Calculation of the Bi^+ substitutional center shows that the crystal lattice is distorted rather slightly: Bi atom lies in the cation site, the nearest Cl atoms are displaced towards Bi atom, and the nearest Tl atoms are displaced

apart from Bi atom, so that Bi–Cl and Bi–Tl distances are 3.120 and 3.889 Å, respectively (3.320 and 3.834 Å in TlCl crystal). A luminescence band is expected to be near 1.0 μm excited in absorption near 0.8, 0.7, and ~ 0.5 μm (Fig. 3(a)). Another one, with much a lower lifetime, may occur near 0.8 μm.

Lattice relaxation turns out to be much more significant in the $\text{Bi}^+ \cdots \text{V}_{\text{Cl}}^-$ complex center. Bi atom is displaced by 1.146 Å from the cation site towards the vacant Cl site, the nearest Cl and Tl atoms are displaced towards Bi atom, and the Tl atoms surrounding Cl vacancy are displaced apart from the vacant site. So the Bi–Cl, Bi–Tl, and Tl– V_{Cl} distances are 3.024, 3.598, and 4.009 Å, respectively, as compared to 3.320, 3.834, and 3.320 Å in TlCl crystal. The relaxation is accompanied by the electron density shifted from Bi atom into the Cl vacancy region, so that the complex center may be thought of as a bound pair of ions, “ Bi^+ plus negatively charged V_{Cl}^- vacancy”. The IR luminescence is expected in the bands near 1.6 and 1.2 μm, both excited in absorption near 0.8, 0.7, and ~ 0.4 μm (Fig. 3(b)). Again a luminescence band with significantly shorter (by an order of magnitude) lifetime may occur near 0.8 μm.

As well our modeling shows that Bi_2^+ dimer centers can occur in TlCl:Bi crystal. Bi atoms are displaced from the adjacent cation sites towards each other, the nearest Cl atoms are displaced towards the dimer, and the nearest Tl atoms are displaced apart from the dimer. The Bi–Bi, Bi–Cl, and Bi–Tl distances are 2.903, 3.060, and 3.960 Å, respectively (3.834, 3.320, and 3.834 Å, respectively, in TlCl crystal). The excess charge, $-1|e|$, turns out to be localized mainly in the Bi atom and marginally in the nearest Cl atoms. So the center is Bi_2^+ dimer indeed. One might expect the luminescence bands near 1.1 and 1.3 μm excited in absorption near 1.1, 0.8, 0.7, 0.5 and ~ 0.4 μm. In one more band at ~ 2.4 μm the luminescence corresponding to the transition from the lowest excited state (Fig. 3(c)) might be observable at a low temperature.

IV. CONCLUSIONS

Our spectroscopic data and results of modeling of Bi-related centers in TlCl:Bi crystal suggest that the near-infrared luminescence in TlCl:Bi is caused mainly by $\text{Bi}^+ \cdots \text{V}_{\text{Cl}}^-$ complexes formed by Bi substitutional ions and intrinsic defects, chlorine vacancies (Fig. 2 and 3(b)). The Bi-related contribution to the total absorption is caused mainly by single Bi^+ substitutional centers not responsible for the IR luminescence (Fig. 1 and 3(a)). So the IR luminescence excitation spectrum (Fig. 2) differs significantly from the absorption spectra of TlCl:Bi samples (Fig. 1). Bi_2^+ dimer complexes in TlCl:Bi can contribute perceptibly neither to the IR luminescence spectra nor to the absorption spectra, as distinct from the assumptions on CsI:Bi crystals [7, 8].

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